

**CARBON AND OXYGEN STABLE ISOTOPE MEASUREMENTS OF MARTIAN ATMOSPHERIC CO<sub>2</sub> BY THE PHOENIX LANDER.** P. B. Niles<sup>1</sup>, W.V. Boynton<sup>2</sup>, J. H. Hoffman<sup>3</sup>, D. W. Ming<sup>1</sup>, D. Hamara<sup>2</sup>, and the Phoenix Science Team, <sup>1</sup>Astromaterials Research and Exploration Science, NASA Johnson Space Center, Houston, TX 77058; <sup>2</sup>Department of Planetary Sciences, University of Arizona, Tucson, AZ, USA; <sup>3</sup>Physics Department, University of Texas, Dallas, TX, USA. (*paul.b.niles@nasa.gov*)

**Introduction:** Precise stable isotope measurements of the CO<sub>2</sub> in the martian atmosphere have the potential to provide important constraints for our understanding of the history of volatiles, the carbon cycle, current atmospheric processes, and the degree of water/rock interaction on Mars [1].

The isotopic composition of the martian atmosphere has been measured using a number of different methods (Table 1), however a precise value (<1%) has yet to be achieved. Given the elevated δ<sup>13</sup>C values measured in carbonates in martian meteorites [2-4] it has been proposed that the martian atmosphere was enriched in <sup>13</sup>C [8]. This was supported by measurements of trapped CO<sub>2</sub> gas in EETA 79001[2] which showed elevated δ<sup>13</sup>C values (Table 1). More recently, Earth-based spectroscopic measurements of the martian atmosphere have measured the martian CO<sub>2</sub> to be depleted in <sup>13</sup>C relative to CO<sub>2</sub> in the terrestrial atmosphere[7, 9-11].

The Thermal and Evolved Gas Analyzer (TEGA) instrument on the Mars Phoenix Lander [12] included a magnetic-sector mass spectrometer (EGA) [13] which had the goal of measuring the isotopic composition of martian atmospheric CO<sub>2</sub> to within 0.5%. The mass spectrometer is a miniature instrument intended to measure both the martian atmosphere as well as gases evolved from heating martian soils.

**Analytical Methods:** Mars atmospheric CO<sub>2</sub> was compared to CO<sub>2</sub> contained in a calibration gas that the instrument carried to Mars, details of analytical methods were described previously [14]. The peak rates were averaged over an analysis period of 1 to 3 mi-

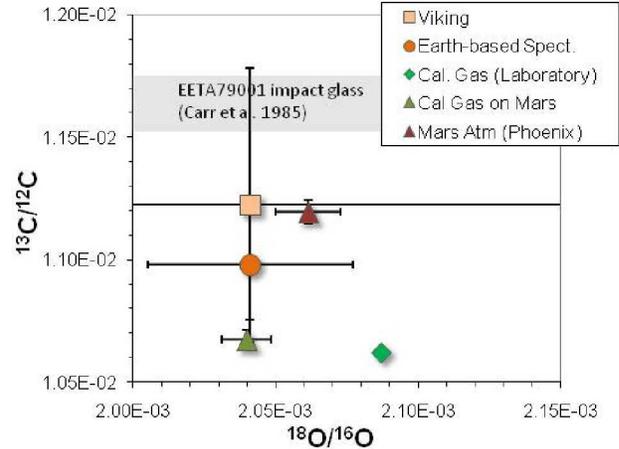


Figure 1. Carbon-Oxygen crossplot. Red triangle shows Phoenix measurement as compared to Viking[5, 6] and Earth based spectroscopy [7]. The green points show comparison of TEGA analysis of calibration gas on Mars and a laboratory analysis. The difference between these points can be used to correct for any instrumental fractionation effects.

utes for masses 44, 45 and 46 collected by TEGA's channel 4 CEM. These averages were corrected for the deadtime of the pre-amplifier discriminator (71 ns). The background measured in the instrument prior to ingesting gas was subtracted, backgrounds were typically below 5% of the signal, but in some cases were as high as 30% when the instrument had been run multiple days in a row. A correction for <sup>17</sup>O in mass 45 was also applied using the terrestrial value for standard mean ocean water (VSMOW) of 0.0003799. Uncertainties

**Table 1.** Reported values for isotopic composition of martian atmospheric CO<sub>2</sub> including results from this study. (VPDB: Vienna Pee Dee Belemnite; VSMOW: Vienna Standard Mean Ocean Water)

Carbon	<sup>13</sup> C/ <sup>12</sup> C	uncertainty	δ <sup>13</sup> C (VPDB) (‰)	uncertainty (‰)	Reference
SNC-Trapped Gas (EETA79001)	0.0116	0.0001	36	10	Carr et al. (1985)
Viking - Neutral MS	0.0111	0.0007	-10	58	Nier and McElroy (1977)
Viking - GC MS	0.0112	0.0006	0	50	Owen et al. (1977)
Atm-Spectroscopy	0.0104	0.0007	-73	58	Schrey et al. (1986)
Atm-Spectroscopy	0.0106	0.0017	-60	150	Krasnopolsky et al. (1996)
Atm-Spectroscopy	0.0112	0.0012	0	110	Encrenaz et al. (2005)
Atm-Spectroscopy	0.0110	0.0002	-22	20	Krasnopolsky et al. (2007)
<b>Phoenix MS</b>	<b>0.01120</b>	<b>0.00005</b>	<b>-2.5</b>	<b>4.3</b>	<b>This study</b>
Oxygen	<sup>18</sup> O/ <sup>16</sup> O	uncertainty	δ <sup>18</sup> O (VSMOW) (‰)	uncertainty (‰)	Reference
Viking-Neutral MS	0.00204	0.00011	18	55	Nier and McElroy (1977)
Viking-GC MS	0.00201	0.00010	0	50	Owen et al. (1977)
Atm-Spectroscopy - CO2	0.00193	0.00024	-40	120	Schrey et al. (1986)
Atm-Spectroscopy - CO2	0.00204	0.00004	18	18	Krasnopolsky et al. (2007)
<b>Phoenix MS</b>	<b>0.002061</b>	<b>0.000011</b>	<b>28.0</b>	<b>5.6</b>	<b>This study</b>

are calculated as 2-sigma based on the standard deviation of 48 atmospheric measurements and 39 calibration gas measurements. Calculated uncertainties do not include potential systematic errors resulting from instrumental non-linearities.

**Results:** The results are plotted in Figure 1 and listed in Table 1. Carbon isotope ratios of martian atmospheric CO<sub>2</sub> (-2.5‰) are similar to terrestrial atmospheric CO<sub>2</sub> (-7‰) while the oxygen isotopic composition (+28.0‰) is significantly lighter than terrestrial atmospheric CO<sub>2</sub> (+41‰). The results reported here are within the uncertainty of most previous isotopic measurements of martian CO<sub>2</sub> with the exception of [2].

**Discussion:** The results reported here confirm that the carbon isotopic composition of martian atmospheric CO<sub>2</sub> is not enriched in <sup>13</sup>C and are in agreement with Krasnopolsky et al. [7]. This result is in contradiction with measurements made on trapped gases in martian meteorites [2]. This may be explained if CO<sub>2</sub> trapped in impact melt glasses incorporated significant amounts of <sup>13</sup>C-rich CO<sub>2</sub> generated from carbonate minerals at the impact site.

Carbonates in martian meteorites are typically very enriched in <sup>13</sup>C and have  $\delta^{13}\text{C}_{\text{VPDB}}$  values near +40‰ [2-4] with some as high as +65‰ [15]. One important exception to this is the younger EETA 79001 which contains carbonates with  $\delta^{13}\text{C}$  value near +10‰ [16]. The heavy isotopic values in the older meteorite carbonates are not consistent with formation from the atmospheric CO<sub>2</sub> measured by Phoenix, however younger carbonates in EETA 79001 are consistent with formation from this reservoir (Fig. 2). In addition, measurements of the  $\Delta^{17}\text{O}$  composition of the carbonates in Nakhilites and ALH84001 suggest they incorporate a significant atmospheric component [17]. One scenario that could possibly explain these conflicting data is an early atmospheric carbon reservoir that had been enriched in <sup>13</sup>C through early hydrodynamic escape [18]. Mantle degassing combined with carbonate formation through martian history lowered the  $\delta^{13}\text{C}$  of the atmospheric CO<sub>2</sub> to its present value. In this scenario ancient <sup>13</sup>C-rich carbonates found in ALH 84001 and the Nakhilites were formed from the early <sup>13</sup>C-rich atmosphere while younger carbonates found in EETA 79001 formed from the modern atmosphere. The lack of large amounts of carbonates in the martian crust and low estimates of mantle degassing [19] could suggest that a heavy CO<sub>2</sub> greenhouse was not present early in martian history.

The oxygen isotopic composition of the atmospheric CO<sub>2</sub> is heavy when compared to the silicates on Mars but is lighter than terrestrial atmospheric CO<sub>2</sub>. Similar to terrestrial CO<sub>2</sub>, it is likely that isotopic composition of martian atmospheric CO<sub>2</sub> is dominated by

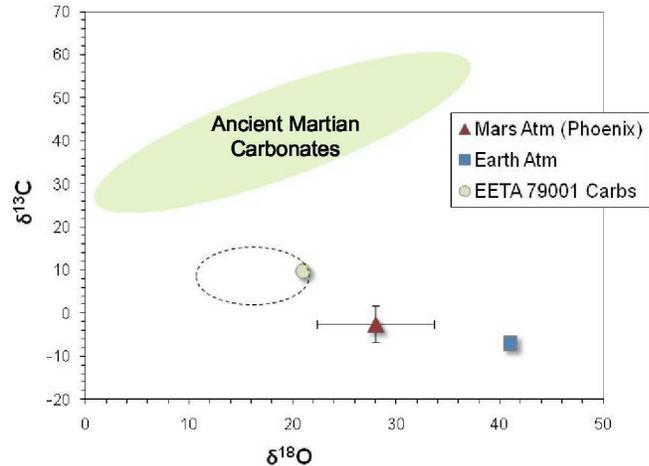


Figure 2. Carbon-oxygen crossplot showing martian atmosphere, terrestrial atmosphere, and martian carbonates. Dotted field shows where carbonates in equilibrium with modern martian atmosphere would appear. Ancient martian carbonates field encompasses analyses of carbonates in ALH 84001 and Nakhilites [2-4].

exchange with liquid water. If this equilibration took place at an average temperature of 0°C, the  $\delta^{18}\text{O}$  of liquid water would be close to -17‰. This is consistent with a measurements of H<sub>2</sub>O(v) depleted in <sup>18</sup>O by Bjoraker [20] using Earth based spectroscopy.

**Conclusions:** The TEGA instrument on the Phoenix spacecraft has made a direct measurement of the isotopic composition of martian atmospheric CO<sub>2</sub> on the surface of Mars to a precision better than 0.5%. Martian atmospheric CO<sub>2</sub> has a  $\delta^{13}\text{C}$  of  $-2.5 \pm 4.3\text{‰}$  and a  $\delta^{18}\text{O}$  of  $+28.0 \pm 5.6\text{‰}$ . This is consistent with the results from the Viking spacecraft [5, 6], Earth based spectroscopic measurements [7], as well as the youngest carbonates preserved in martian meteorites [16] and has wide implications for understanding the past and current climate history of Mars.

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